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Syntheses, Structures, and Catalytic Activities of the Anionic Heterobimetallic Rare-Earth Metal Complexes Supported by Pyrrolyl-Substituted 1,2-Diimino Ligands

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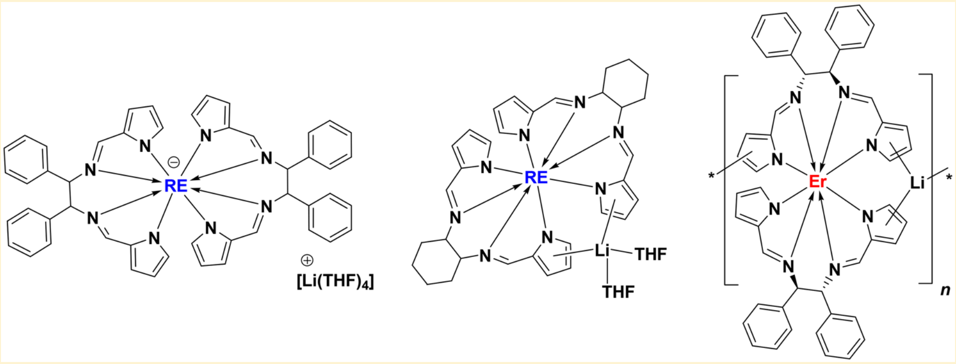
Supporting Information



ABSTRACT: A series of the anionic heterobimetallic rare-earth metal complexes supported by *trans*- or chiral pyrrolyl-substituted 1,2-diimino ligands were synthesized in good yields via reactions of $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ with the corresponding 1,2-diimino proligands. Reactions of $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ with 2 equiv of *trans*-1,2-bis(pyrrol-2-ylmethylene)-1,2-diphenylethanediamine ($\mathbf{H_2L^1}$) afforded the discrete ion-pair rare-earth metal complexes $[Li(THF)_4]^+[(\mathbf{L^1})_2RE]^-$ (RE = Sm(**5**), Dy(**6**), Er(**7**)). Reactions of $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ with 2 equiv of (*R*,*R*)-1,2-bis(pyrrol-2-ylmethylene)-1,2-diphenylethanediamine ($\mathbf{H_2L^2}$) gave the heterobimetallic rare-earth metal complexes $(\mathbf{L^2})_2RELi(THF)_2$ (RE = Sm(**8**), Y(**9**)). When the rare-earth metal is Er, the chiral linear rare-earth coordination polymer $\{(\mathbf{L^2})_2ErLi\}_n$ (**10**) was obtained. Reactions of $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ with 2 equiv of *trans*-1,2-bis(pyrrol-2-ylmethyleneamino)cyclohexane ($H_2\mathbf{L^3}$) gave the heterobimetallic rare-earth metal complexes $(\mathbf{L^3})_2RELi(THF)_2$ (RE = Pr (**11**), Sm(**12**), Eu(**13**)). Reactions of $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ with 2 equiv of (*R*,*R*)-1,2-bis(pyrrol-2-ylmethyleneamino)-cyclohexane ($H_2\mathbf{L^4}$) also gave the heterobimetallic rare-earth metal complexes $(\mathbf{L^4})_2RELi(THF)_2$ (Ln = Pr(**14**), Sm(**15**)). All complexes were characterized by spectroscopic methods and elemental analyses, and complexes **5**−**11**, **13**, and **14** were further determined by single-crystal X-ray diffraction. The catalytic properties of racemic rare-earth metal complexes on cyanosilylation of ketones were examined, and results showed that the above complexes could effectively catalyze the cyanosilylation of ketones. Chiral rare-earth metal complexes as catalysts for the enantioselective epoxidation of α,β-unsaturated ketones were also examined to afford the chiral epoxides in high yields with moderate enantioselectivities.

■ INTRODUCTION

Heterobimetallic rare-earth metal alkylaluminate complexes have attracted wide attention as the efficient olefin polymerization catalysts due to their similarity to Ziegler−Natta systems.[1] Though rare-earth metal heterobimetallic complexes bearing Group 1 metals such as lithium and potassium have also been developed for various transformation,[2] the systematically synthetic method for this type of heterobimetallic complexes needs to be developed. Dianionic ligands, such as the chelating diamido ligands,[3] boraamidinate,[4] bis(allyl)-silane,[5] linked amido-cyclopentadienyl or indenyl-pyrrolyl ligands,[6] bisphenolate and binaphtholates,[7] binaphthylamido ligands,[8] phenoxy-amidinate ligands,[9] etc. have proved to be particularly useful in the formation of heterobimetallic lanthanide complexes. Salen-type Schiff-base ligands also have a tendency to form the heterobimetallic lanthanide complexes, especially, when the backbone of Salen ligand was chiral diamine, the resulting chiral rare-earth metal complexes

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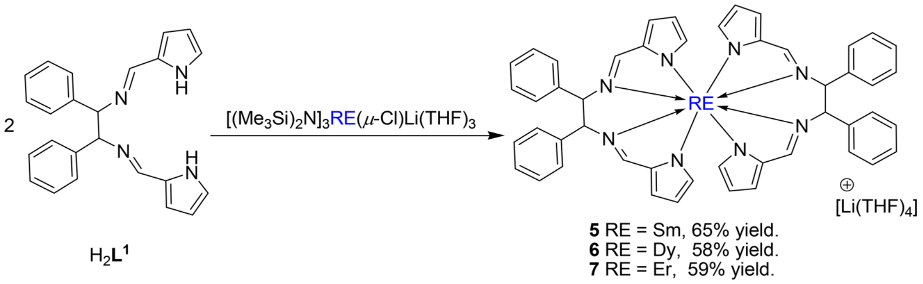
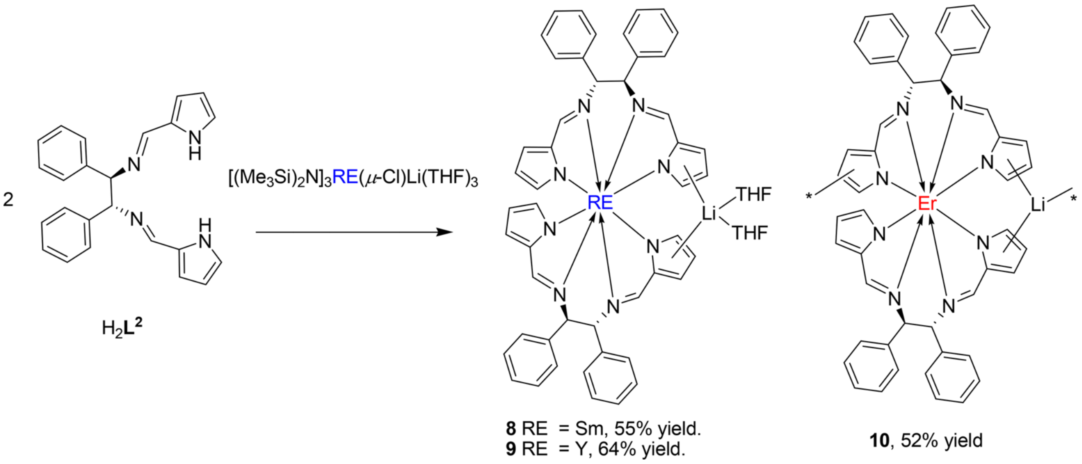
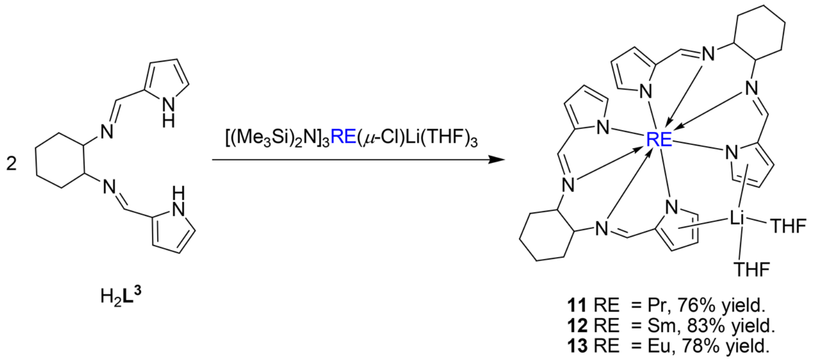
Scheme 1. Synthesis of Complexes 5−7



Scheme 2. Synthesis of Complexes 8−10



Scheme 3. Synthesis of Complexes 11−13



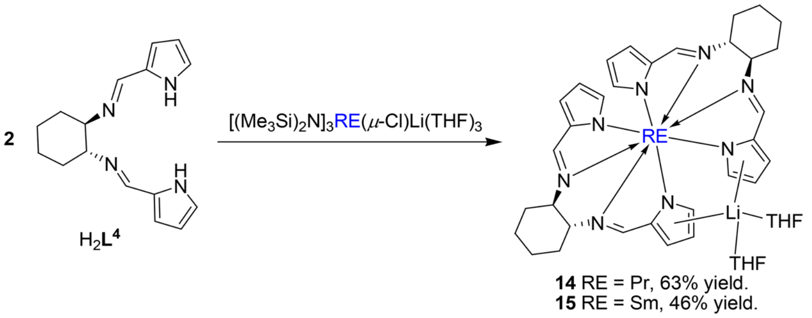
exhibited the good catalytic activities for asymmetric transformation or stereoselective polymerization.[10]

Pyrrolyl-substituted Schiff-base ligands have widely been applied to organolanthanide chemistry;[11] however, heterobimetallic rare-earth metal complexes containing pyrrolyl-substituted diimino ligands still needs to be developed.[12] Pyrrolyl-substituted 1,1′-bi-2-naphthylamino rare-earth metal complexes have been studied as catalysts for asymmetric hydroamination of alkenes.[12a] The heterobimetallic rare-earth metal and uranium complexes bearing a binucleating polypyrrole Schiff-base ligand showed magnetic bistability at 3 K, a property required for the development of single-molecule magnets.[12d] Anionic heterobimetallic rare-earth metal complexes supported by a pyrrole-based substituted diimino ligand have been demonstrated as catalysts toward the polymerization of ε-caprolactone.[12c] Herein, we will report the preparation and characterization of the rare-earth metal complexes containing pyrrolyl-substituted diimino ligands, as expected, the anionic heterobimetallic rare-earth metal complexes were obtained. Their catalytic activities in the cyanosilylation of ketones and the enantioselective epoxidation of chalcones will also be reported.

■ RESULTS AND DISCUSSION

Synthesis and Characterization. The *trans*- or chiral pyrrolyl-substituted 1,2-diimines H_2L^1−H_2L^4 were synthesized through condensation of pyrrole-2-carboxyaldehyde with the corresponding *trans*- or chiral 1,2-diamino ligands under a catalytic amount of TsOH according to the published procedure.[13] Reaction of $[(Me_3Si)_2N]_3RE(\mu\text{-Cl})Li(THF)_3$ with 2 equiv of H_2L^1 afforded the discrete ion-pair heterobimetallic rare-earth metal complexes $[Li(THF)_4]^+[(L^1)_2RE]^-$ (RE = Sm(**5**), Dy(**6**), Er(**7**)) (Scheme 1). However, reaction of $[(Me_3Si)_2N]_3RE(\mu\text{-Cl})Li(THF)_3$

Scheme 4. Synthesis of Complexes 14 and 15



14 RE = Pr, 63% yield.
15 RE = Sm, 46% yield.

with 2 equiv of $H_2\mathbf{L}^2$ gave the chiral heterobimetallic rare-earth metal complexes $(\mathbf{L}^2)_2$RELi(THF)$_2$ (RE = Sm(**8**), Y(**9**)) (Scheme 2). It is noteworthy that the chiral linear rare-earth coordination polymer $\{(\mathbf{L}^2)_2\mathrm{ErLi}\}_n$ (**10**) was obtained when rare-earth metal is Er (Scheme 2). Reactions of $[(Me_3Si)_2N]_3RE(\mu\text{-Cl})Li(THF)_3$ with 2 equiv of $H_2\mathbf{L}^3$, different from pyrrolyl-substituted *trans*-1,2-diphenylethylenediamine, gave the heterobimetallic rare-earth metal complexes $(\mathbf{L}^3)_2$RELi(THF)$_2$ (RE = Pr(**11**), Sm(**12**), Eu(**13**)) (Scheme 3). Reactions of $[(Me_3Si)_2N]_3RE(\mu\text{-Cl})Li(THF)_3$ with 2 equiv of $H_2\mathbf{L}^4$ gave the chiral heterobimetallic rare-earth complexes $(\mathbf{L}^4)_2$RELi(THF)$_2$ (RE = Pr(**14**), Sm(**15**)) (Scheme 4). Complexes **5**−**15** are extremely sensitive to air and moisture. They are soluble in THF and toluene and slightly soluble in *n*-hexane. All complexes were fully characterized by spectroscopic methods and elemental analyses. The structures of complexes **5**−**11**, **13**, and **14** were further determined by single-crystal X-ray analyses.

The molecular structures of complexes **5**−**11**, **13**, and **14** were determined by the single-crystal X-ray diffraction. As expected, a series of the anionic heterobimetallic rare-earth metal complexes were obtained. X-ray analyses revealed that complexes **5**−**7** were isostructural discrete ion-pair rare-earth metal complexes, and a representative structure diagram of complex **6** is shown in Figure 1. Chiral complexes **8** and **9** were heterobimetallic rare-earth metal complexes, and a representative structure diagram of complex **9** is shown in Figure 2. Complex **10** was the chiral linear rare-earth metal coordination polymer, and the structure diagram is shown in Figure 3. Rare-earth metal complexes **11** and **13** containing *trans*-1,2-bis(pyrrol-2-ylmethyleneamino)cyclohexane were isostructural heterobimetallic rare-earth metal complexes, and a representative structure diagram of complex **11** is shown in Figure 4. The corresponding chiral complex **14** (Figure 5) was also heterobimetallic rare-earth metal complex. The selected bond distances and angles are listed in Tables 1 and 2.

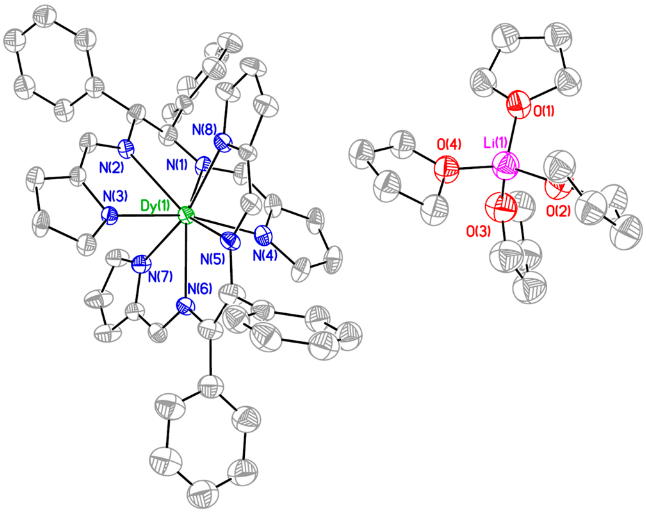


Figure 1. Representative molecular structure of complex **6**. Hydrogen atoms are omitted for clarity.

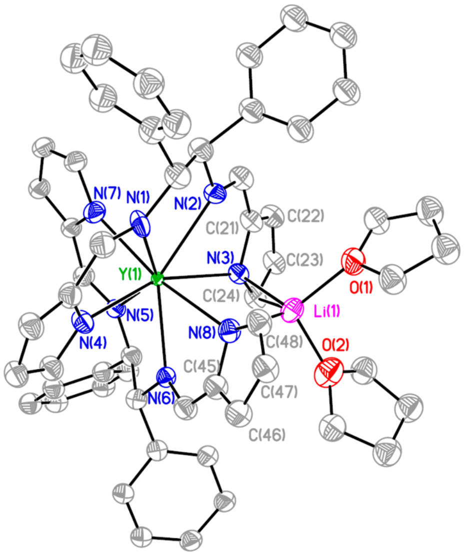


Figure 2. Representative molecular structure of complex **9**. Hydrogen atoms are omitted for clarity.

X-ray analyses revealed that each RE^{3+} is bound to four nitrogen atoms from the two ligands which are perpendicular to each other, and the Li ion adopts tetrahedral geometry. From Tables 1 and 2, the average RE(1)−N bond distances are also consistent with the trend in ionic radius of the corresponding elements. The average RE(1)−N bond length in discrete ion-pair rare-earth metal complexes was slightly shorter than those in the heterobimetallic rare-earth metal complexes, for example, Sm(1)−N_{av} of 2.529(5) Å in complex **5** vs 2.537(4) Å in complex **8** and Er(1)−N_{av} of 2.466(8) Å in complex **7** vs 2.473(4) Å in complex **10**. These RE−N bond lengths are also comparable with the RE−N bond length in the reported (*R*)-bis(pyrrol-2-ylmethyleneamino)-1,1′-binaphthyl rare-earth metal complexes.[12a,b]

X-ray analyses revealed that the coordination modes between lithium and pyrrolyl group were affected by different rare-earth metals and ligands. In complexes **8** and **9**, two pyrrolyl groups coordinated to lithium in η^2-modes. In complex **10**, one pyrrolyl group coordinated to lithium in η^2-

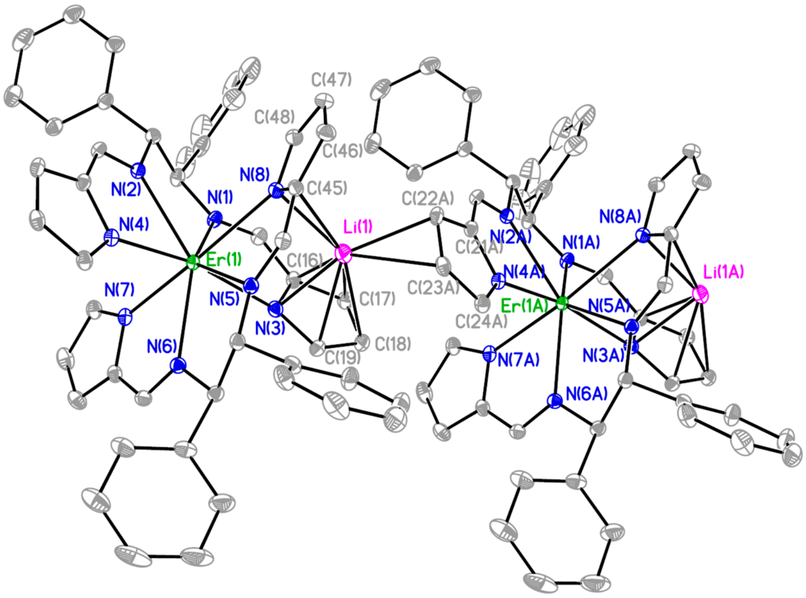


Figure 3. Molecular structure of complex **10**. Hydrogen atoms are omitted for clarity.

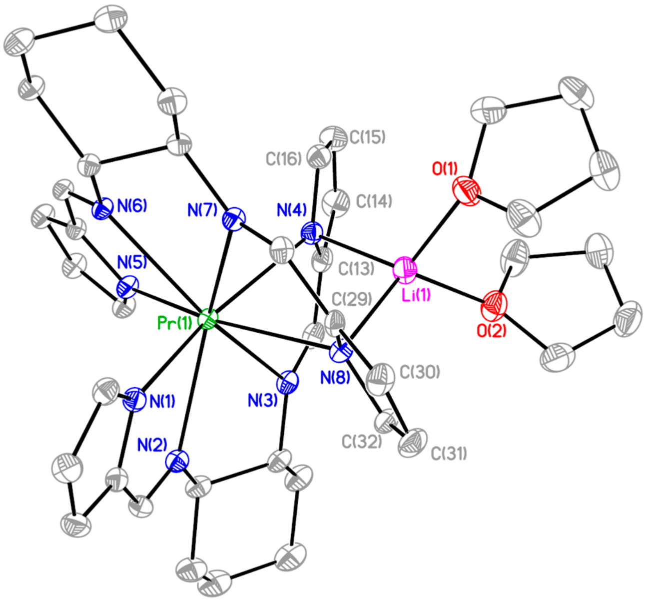


Figure 4. Representative molecular structure of complex **11**. Hydrogen atoms are omitted for clarity.

modes, and the other coordinated to lithium in η^5-modes. In complexes **11**, **13**, and **14**, two pyrrolyl groups coordinated to lithium in η^1-modes. From bond angles of complexes in Tables 1 and 2, the sums of N(1)−RE(1)−N(2), N(2)−RE(1)−N(3), N(3)−RE(1)−N(4), and N(1)−RE(1)−N(4) in discrete ion-pair complexes **5**−**7** were 359.71°−360.14°, indicating that the atoms of Er(1) and N(1)−N(4) are nearly planar, which were further demonstrated by rms deviation of fitted atoms of Er(1) and N(1)−N(4) from the corresponding least-squares planes being less than 0.070 as are the atoms of Er(1) and N(5)−N(8). However, in heterobimetallic complexes **8**−**11**, **13**, and **14**, the sums of N(1)−RE(1)−N(2), N(2)−RE(1)−N(3), N(3)−RE(1)−N(4), and N(1)−RE(1)−N(4) deviate farther from 360° degrees, indicating that the atoms of N(1)−N(4) or N(5)−N(8) were slightly distorted in the heterobimetallic rare-earth metal complexes.

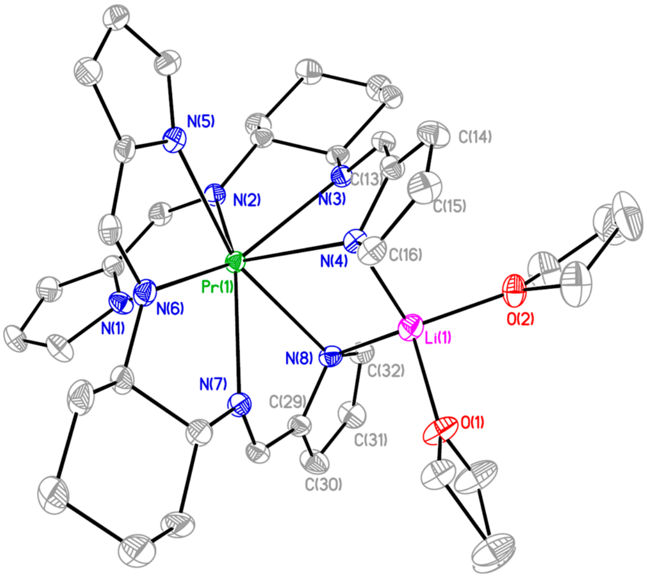


Figure 5. Molecular structure of complex **14**. Hydrogen atoms are omitted for clarity.

These differences may be owing to the different coordination modes caused by the direct incorporation of Li ions in the latter.

Catalytic Additions of Trimethylsilyl Cyanide to Ketones. Rare-earth metal complexes as catalysts for the addition or enantioselective addition of Me_3SiCN to carbonyl compounds have been developed.[14] Recently, rare-earth-polyoxometalates as Lewis acid−base catalysts have also showed great potential for cyanosilylation of carbonyl compounds.[15] Herein, the above heterobimetallic complexes supported by *trans*- or chiral pyrrolyl-substituted 1,2-diimino ligands were examined for the addition or enantioselective addition of Me_3SiCN to ketones. The enantioselective addition of Me_3SiCN to acetophenone was first investigated as the template reaction in the presence of 1 mol % of rare-earth metal complexes supported by chiral pyrrolyl-substituted 1,2-diimino ligands. The reactions underwent rapidly to provide

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) of Complexes 5−10

	5 (Sm)	**6** (Dy)	**7** (Er)	**8** (Sm)	**9** (Y)	**10** (Er)
RE(1)−N(1)	2.541(5)	2.506(6)	2.500(7)	2.530(4)	2.511(10)	2.492(4)
RE(1)−N(2)	2.541(4)	2.509(6)	2.506(6)	2.525(4)	2.530(12)	2.518(4)
RE(1)−N(3)	2.503(5)	2.462(6)	2.427(6)	2.570(5)	2.578(11)	2.442(4)
RE(1)−N(4)	2.509(5)	2.452(5)	2.429(5)	2.490(4)	2.504(11)	2.465(4)
RE(1)−N(5)	2.555(5)	2.508(7)	2.487(7)	2.537(5)	2.511(10)	2.499(4)
RE(1)−N(6)	2.561(5)	2.499(6)	2.500(6)	2.549(4)	2.516(10)	2.466(4)
RE(1)−N(7)	2.512(5)	2.472(7)	2.442(7)	2.484(5)	2.474(12)	2.395(4)
RE(1)−N(8)	2.509(5)	2.474(7)	2.436(7)	2.607(4)	2.526(12)	2.506(4)
RE(1)−N_{av}	2.529(5)	2.485(7)	2.466(7)	2.537(5)	2.519(12)	2.473(4)
Li(1)−N(3)				2.171(9)	2.15(3)	2.152(11)
Li(1)−N(8)				2.138(8)	2.20(3)	2.231(12)
Li(1)−C(16)						2.302(12)
Li(1)−C(17)						2.549(12)
Li(1)−C(18)						2.532(12)
Li(1)−C(19)				2.776(12)	2.71(3)	2.292(12)
Li(1)−C(48)				2.754(11)	2.80(3)	
Li(1)−C(45)						2.765(13)
Li(1)−C(22)#A						2.338(11)
Li(1)−C(23)#A						2.623(12)
Li(1)−O(1)	1.88(2)	1.85(3)	1.92(3)	1.968(12)	2.01(3)	
Li(1)−O(2)	1.90(2)	1.97(3)	1.84(3)	1.987(12)	1.91(3)	
Li(1)−O(3)	1.89(2)	1.89(3)	1.85(3)			
Li(1)−O(4)	1.94(2)	1.87(3)	1.93(3)			
N(1)−RE(1)−N(2)	62.19(15)	63.3(2)	63.6(3)	63.19(14)	63.1(4)	63.61(13)
N(2)−RE(1)−N(3)	66.76(15)	66.3(2)	67.5(2)	65.68(14)	66.7(4)	67.54(14)
N(3)−RE(1)−N(4)	164.32(16)	163.8(2)	162.0(3)	166.27(14)	158.9(4)	161.91(14)
N(4)−RE(1)−N(1)	66.44(16)	66.7(2)	67.0(3)	66.62(14)	67.0(4)	67.50(13)
N(5)−RE(1)−N(6)	62.45(16)	62.5(2)	63.2(2)	63.24(17)	62.7(3)	64.27(13)
N(6)−RE(1)−N(7)	66.22(14)	67.8(2)	67.5(3)	66.90(17)	67.2(3)	69.92(14)
N(7)−RE(1)−N(8)	165.34(16)	162.9(2)	162.3(3)	159.50(16)	165.1(4)	157.80(14)
N(5)−RE(1)−N(8)	66.13(17)	66.6(2)	67.0(3)	65.50(15)	66.4(3)	66.04(14)

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of Complexes 11, 13, and 14

	11 (Pr)	**13** (Eu)	**14** (Pr)
RE(1)−N(1)	2.548(3)	2.491(9)	2.518(6)
RE(1)−N(2)	2.579(3)	2.532(9)	2.575(5)
RE(1)−N(3)	2.623(3)	2.572(10)	2.597(5)
RE(1)−N(4)	2.593(3)	2.530(9)	2.623(6)
RE(1)−N(5)	2.538(3)	2.493(9)	2.511(5)
RE(1)−N(6)	2.555(2)	2.496(9)	2.589(5)
RE(1)−N(7)	2.619(2)	2.558(9)	2.608(4)
RE(1)−N(8)	2.597(3)	2.534(9)	2.653(5)
RE(1)−N_{av}	2.582(3)	2.526(10)	2.584(6)
Li(1)−N(4)	2.113(7)	2.14(2)	2.109(13)
Li(1)−N(8)	2.111(7)	2.11(2)	2.168(17)
Li(1)−O(1)	1.958(7)	2.00(2)	1.963(12)
Li(1)−O(2)	1.989(7)	1.97(2)	1.962(14)
N(1)−RE(1)−N(2)	65.84(9)	67.1(3)	66.19(17)
N(2)−RE(1)−N(3)	61.79(9)	63.0(3)	62.70(17)
N(3)−RE(1)−N(4)	64.95(9)	65.7(3)	64.20(17)
N(1)−RE(1)−N(4)	157.29(9)	156.0(3)	167.35(17)
N(5)−RE(1)−N(6)	66.34(8)	67.5(3)	66.47(17)
N(6)−RE(1)−N(7)	62.27(8)	63.2(3)	61.89(15)
N(7)−RE(1)−N(8)	64.91(8)	65.5(3)	63.43(14)
N(5)−RE(1)−N(8)	158.41(9)	157.1(3)	162.79(18)

the cyanosilylation products in high yields, but unfortunately, the products are almost *racemic*. Next, we examined rare-earth metal complexes supported by *trans*-pyrrolyl-substituted 1,2-diimino ligands, and optimizations of the catalytic activity were listed in Table 3. The cyanosilylation of acetophenone could be accomplished in various solvents at room temperature within 4 h, affording the product in >90% yields with a 0.01 mol % catalyst loading (Table 3, entries 6−8). It was further found that a high yield of product **17a** could be also obtained under solvent-free conditions using rare-earth metal complexes **5**−**7** and **11**−**13** as catalysts (Table 3, entries 9−14). Results also showed that both the discrete ion-pair and heterobimetallic rare-earth metal complexes are capable of catalyzing the cyanosilylation of ketone under the mild conditions with low catalyst loadings.

So, complex **5** or **12** was selected as the catalyst for the following experiments to examine the scope of the cyanosilylation reaction of ketones, and the results are presented in Table 4. Results showed that various aromatic ketones bearing either electron-donating (CH_3, OMe) or electron-withdrawing groups (Cl, Br, NO_2) underwent cyanosilylation to produce the expected products in good to excellent yield (86−99%). It seems that the sterics of the substrates have neglectable effect on the reaction (entries 2−3, 5−6, 8−10, and 11), further indicating the high efficiency of the catalysts. Notably, aliphatic ketones, either cyclic or acyclic,

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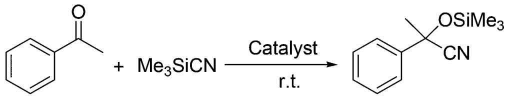
Table 3. Optimization of Cyanosilylation of Acetophenone[a]



16a **17a**

entry	catalyst	loading (mol %)	time (h)	solvent	yield (%)[b]
1	7	1	0.5	toluene	74
2	7	1	1	toluene	85
3	7	1	2	toluene	92
4	7	0.1	4	toluene	97
5	7	0.05	4	toluene	95
6	7	0.01	4	toluene	95
7	7	0.01	4	Et_2O	92
8	7	0.01	4	THF	97
9	7	0.01	4	solvent free	97
10	**5**	0.01	4	solvent free	99
11	**6**	0.01	4	solvent free	98
12	**11**	0.01	3	solvent free	97
13	**12**	0.01	3	solvent free	99
14	**13**	0.01	3	solvent free	96

[a] Conditions: acetophenone (5.0 mmol), Me_3SiCN (6.0 mmol), solvent (2.0 mL) or solvent free, room temperature. [b] Isolated yields.

also afforded the cyanosilylation products in nearly quantitative yields (entries 12–14).

Enantioselective Epoxidation of *α,β*-Unsaturated Ketones. Despite the wealth of catalytic enantioselective epoxidations of *α,β*-unsaturated ketones, rare-earth complexes as catalysts still need to be further developed.[7a] Very recently, a strategy for the enantioselective epoxidation of *α,β*-unsaturated ketones employing a heterobimetallic rare-earth-lithium complex bearing a phenoxy-functionalized diphenylprolinolate ligand has been developed.[16] So, we tested the heterobimetallic rare-earth metal complexes for the enantioselective epoxidation of chalcones, and results are listed in Table 5. Results showed that the heterobimetallic rare-earth metal complexes supported by a chiral pyrrolyl-substituted 1,2-diphenyldiimino ligand were superior to those bearing a chiral pyrrolyl-substituted 1,2-cyclohexanyl diimino ligand (entries 1–5, Table 5). The moderate enantioselectivity of 57% ee was obtained by employing complex **9** as catalyst (entry 2, Table 5). Further optimizations revealed that lowering the temperature slightly improved the enantioselectivity to 63% ee (entry 9, Table 5). Next, complex **9** was selected as the catalyst for the enantioselective epoxidation of *α,β*-unsaturated ketones bearing halide, methyl, and methoxy groups, and the corresponding products **19a–19e** were obtained in moderate enantioselectivities of 57–65% ee with good yields (entries 1–5, Table 6).

CONCLUSION

In conclusion, a series of the anionic heterobimetallic rare-earth metal complexes supported by *trans-* or chiral pyrrolyl-substituted 1,2-diimino ligands were systematically synthesized via reactions of $[(Me_3Si)_2N]_3RE(\mu\text{-Cl})Li(THF)_3$ with the corresponding 1,2-diimino ligands. X-ray diffraction revealed that they separately belonged to the two types of the discrete ion-pair or heterobimetallic rare-earth metal complexes. The racemic heterobimetallic rare-earth metal complexes showed high catalytic activity for the cyanosilylation of ketones. Chiral heterobimetallic rare-earth metal complexes as catalysts for the enantioselective epoxidation of *α,β*-unsaturated ketones afforded the chiral epoxides in good yields with moderate enantioselectivities.

EXPERIMENTAL SECTION

General Remarks. All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and oxygen-free atmosphere using standard Schlenk techniques or in a glovebox. Solvents were refluxed and distilled over sodium/benzophenone under argon prior to use. $[(Me_3Si)_2N]_3RE(\mu\text{-Cl})Li(THF)_3$ (RE = Sm, Eu, Dy, Y, Er),[17] *trans*-1,2-bis(pyrrol-2-ylmethyleneamino)cyclohexane,[13] and (*R*,*R*)-1,2-bis(pyrrol-2-ylmethyleneamino)cyclohexane[18] were prepared according to literature methods. IR spectra were recorded on a SHIMADZU FTIR-8400S spectrometer. ^1H NMR and ^{13}C NMR spectra for analyses of compounds were recorded on a Bruker AV-300 NMR or AV-500 NMR spectrometer in C_6D_6 for rare-earth complexes and in $CDCl_3$ for organic compounds.

Synthesis of Compounds H_2L^1 or H_2L^2. Pyrrole-2-carbaldehyde (1.90 g, 20 mmol) and either *trans-* or (*R*,*R*)-1,2-diphenylethylenediamine (2.12 g, 10.0 mmol) were dissolved in ethanol (30.0 mL). The mixture was stirred, and then a few drops of TsOH were added. After the reaction mixture was stirred for 3 h, the precipitate obtained from filtration was washed with hexane, dried in vacuum, and crystallized from CH_3CH_2OH. Compound $H_2\mathbf{L}^1$ (3.08 g, 84% yield) or $H_2\mathbf{L}^2$ (2.93 g, 80% yield) was obtained. ^1H NMR (500 MHz, $CDCl_3$): δ 7.92 (s, 2H), 7.21–7.08 (m, 10H), 6.83 (s, 2H), 6.35–6.33 (m, 2H), 6.17–6.14 (m, 2H), 4.64 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.5, 141.8, 130.3, 128.0, 126.9, 121.7, 114.5, 109.6, 80.3. HR-MS (ESI) Calcd for $C_{24}H_{22}N_4$ [M + H$^+$]: 367.1917, found: 367.1913.

General Synthesis of $[Li(THF)_4]^+[(L_1)_2RE]^-$ (RE = Sm(5), Dy(6), Er(7)). Under an argon atmosphere, an oven-dried 50.0 mL Schlenk flask equipped with a magnetic stir bar was charged with the compound $H_2\mathbf{L}^1$ (0.44 g, 1.20 mmol), $[(Me_3Si)_2N]_3RE(\mu\text{-Cl})Li(THF)_3$ (0.60 mmol), and THF (30.0 mL) at room temperature. After the reaction mixture was stirred at 60 °C for 12 h, the solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (10.0 mL), and the resulting solid was extracted with toluene (2 × 15.0 mL). The extractions were combined and concentrated to about 15.0 mL. The crystals were obtained by cooling the concentrated solution at 0 °C for several days.

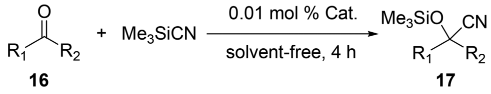
*Complex **5**.* Pale yellow crystals (0.46 g, 65% yield). Mp 216–218 °C. IR (KBr pellets, cm^{-1}): ν 3028 (w), 2976 (m), 2868 (m), 1631 (s), 1597 (m), 1489 (m), 1452 (m), 1392 (s), 1311 (s), 1267 (s), 1031 (s), 974 (s), 810 (m), 740 (s), 700 (s), 604 (m). Anal. Calcd for $C_{64}H_{72}N_8O_4SmLi$: C, 65.44; H, 6.18; N, 9.54; Found: C, 65.78; H, 5.88; N, 9.66.

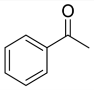
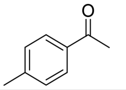
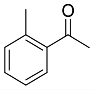
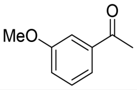
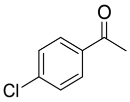
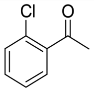
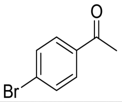
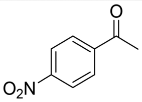
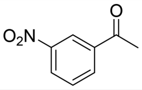
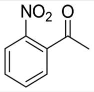
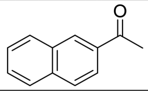
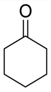
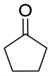
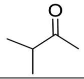
*Complex **6**.* Colorless crystals (0.41 g, 58% yield). Mp 211–213 °C. IR (KBr pellets, cm^{-1}): ν 3028 (w), 2968 (m), 2876 (m), 2360 (m), 2330 (m), 1629 (s), 1597 (s), 1497 (s), 1448 (s), 1390 (s), 1311 (m), 1031 (m), 974 (m), 889 (m), 806 (m), 738 (w), 700 (m), 613 (m). Anal. Calcd for $C_{64}H_{72}N_8O_4DyLi$: C, 64.77; H, 6.12; N, 9.44; Found: C, 64.98; H, 5.95; N, 9.56.

*Complex **7**.* Pale yellow crystals (0.42 g, 59% yield). Mp 216–218 °C. IR (KBr pellets, cm^{-1}): ν 3024 (w), 2968 (m), 2875 (m), 1631 (s), 1597 (s), 1489 (s), 1452 (s), 1433 (s), 1392 (s), 1311 (m), 1267 (m), 1180 (m), 1031 (s), 974 (m), 889 (m), 810 (m), 740 (m), 700 (m), 613 (m). Anal. Calcd for $C_{64}H_{72}N_8O_4ErLi$: C, 64.51; H, 6.09; N, 9.40; Found: C, 64.15; H, 5.78; N, 9.58.

General Synthesis of $(L_2)_2RELi(THF)_2$ (RE = Sm(8), Y(9)). Under an argon atmosphere, an oven-dried 50.0 mL Schlenk flask equipped with a magnetic stir bar was charged with the compound $H_2\mathbf{L}^2$ (0.44 g, 1.20 mmol), $[(Me_3Si)_2N]_3RE(\mu\text{-Cl})Li(THF)_3$ (0.60 mmol), and THF (30.0 mL) at room temperature. After the reaction mixture was stirred at 60 °C for 12 h, the solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (10.0 mL), and the resulting solid was extracted with toluene (2 × 15.0 mL). The extractions were combined and concentrated to about 15.0

Table 4. Cyanosilylation of Various Ketones Catalyzed by Complex 5[a]



entry	ketone	product	yield (%)[b]
1		**17a**	99
2		**17b**	98 (95)[c]
3		**17c**	96 (98)[c]
4		**17d**	99
5		**17e**	98 (98)[c]
6		**17f**	95 (96)[c]
7		**17g**	97
8		**17h**	98 (95)[c]
9		**17i**	86
10		**17j**	94 (92)[c]
11		**17k**	99
12		**17l**	98
13		**17m**	99
14		**17n**	99

[a]Conditions: catalyst (0.0005 mmol), ketone (5.0 mmol), Me_3SiCN (6.0 mmol), room temperature. [b]Isolated yields. [c]The yields were obtained using complex **12** as catalyst, time: 3 h.

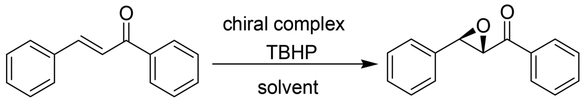
mL. The crystals were obtained by cooling the concentrated solution at 0 °C for several days.

Complex 8. Pale yellow crystals (0.34 g, 55% yield). Mp 227−229 °C. IR (KBr pellets, cm^{-1}): ν 3080 (w), 3021 (w), 2961 (m), 2876 (m), 2364 (w), 1624 (s), 1595 (m), 1497 (m), 1456 (m), 1433 (m), 1388 (s), 1118 (m), 1095 (m), 1033 (m), 1029 (m), 970 (m), 806 (m), 698 (s), 609 (s). Anal. Calcd for $C_{56}H_{56}N_8O_2SmLi$: C, 65.28; H, 5.48; N, 10.87; Found: C, 64.95; H, 5.95; N, 10.56.

Complex 9. Colorless crystals (0.37 g, 64% yield). Mp 236−238 °C. ^1H NMR (500 MHz, C_6D_6): δ 7.86 (m, 8H), 7.27−6.87 (m, 20H), 6.58 (m, 8H), 5.70 (m, 4H), 3.05 (m, 8H), 1.10 (m, 8H). ^{13}C NMR (125 MHz, C_6D_6): δ 160.4, 158.4, 140.4, 136.9, 129.9, 127.6, 125.7, 119.6, 119.1, 111.9, 76.0, 74.3, 68.2, 25.4, 21.5. IR (KBr pellets, cm^{-1}): ν 3080 (w), 3028 (w), 2976 (m), 2876 (m), 2360 (w), 1616 (s), 1595 (m), 1431 (s), 1388 (s), 1267 (m), 1160 (m), 1031 (m), 972 (m), 893 (w), 806 (m), 700 (s), 609 (s). Anal. Calcd for $C_{56}H_{56}N_8O_2YLi$: C, 69.42; H, 5.83; N, 11.56. Found: C, 69.92 ; H, 5.65; N, 11.08.

Synthesis of $\{(L^2)_2ErLi\}_n$ (10). Complex **10** was prepared as pale yellow crystals in a 52% yield from reaction of $[(Me_3Si)_2N]_3Er(\mu\text{-}Cl)Li(THF)_3$ (0.55 g, 0.60 mmol) with the compound H_2L^2 (0.44 g, 1.20 mmol) by employing the procedures similar to those used for

Table 5. Optimization of the Enantioselective Epoxidation of α,β-Unsaturated Ketone[a]



18a **19a**

entry	catalyst	temp (°C)	solvent	time (h)	yield (%)	ee (%)[c]
1	**8**	0	THF	6	87	53
2	**9**	0	THF	6	89	57
3	**10**	0	THF	6	84	39
4	**14**	0	THF	10	88	11
5	**15**	0	THF	4	95	13
6	**9**	0	toluene	10	85	8
7	**9**	0	CH_3CN	10	70	6
8	**9**	−20	THF	6	74	61
9	**9**	−40	THF	6	65	63

[a] Conditions: catalyst (0.1 mmol), chalcone (1.0 mmol), TBHP (*tert*-butyl hydroperoxide) (1.2 mmol), solvent (2.0 mL). [b] Isolated yields. [c] Enantiomeric excess was determined by the HPLC analysis by using the chiral column.

preparation of complexes **8** and **9**. Mp 215−217 °C. IR (KBr pellets, cm^{-1}): ν 3088 (m), 3028 (m), 2968 (m), 2884 (m), 2360 (w), 1620 (s), 1598 (s), 1493 (m), 1452 (m), 1437 (m), 1390 (s), 1311 (s), 1029 (m), 893 (m), 810 (m), 700 (s), 609 (s). Anal. Calcd for $C_{48}H_{40}N_8ErLi$: C, 64.52; H, 5.41; N, 11.15; Found: C, 64.17; H, 5.47; N, 10.85.

General Synthesis of $(L^3)_2$RELi(THF)$_2$ (RE = Pr(11), Sm(12), Eu(13)). Under an argon atmosphere, an oven-dried 50.0 mL Schlenk flask equipped with a magnetic stir bar was charged with the compound H_2L^3 (0.32 g, 1.20 mmol), $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (0.60 mmol), and THF (30.0 mL) at room temperature. After the reaction mixture was stirred at 60 °C for 12 h, the solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (10.0 mL), and the resulting solid was extracted with toluene (2 × 15.0 mL). The extractions were combined and concentrated to about 15.0 mL. The crystals were obtained by cooling the concentrated solution at 0 °C for several days.

Complex 11. Colorless crystals (0.46 g, 76%). Mp 214−216 °C. IR (KBr pellets, cm^{-1}): ν 2933 (w), 1583 (s), 1416 (m), 1313 (m), 1043 (m), 885 (s), 838 (w), 745 (m), 625 (s). Anal. Calcd for $C_{40}H_{52}N_8O_2PrLi\cdot0.5C_7H_8$: C, 60.00; H, 6.48; N, 12.87. Found: C, 60.35; H, 6.47; N, 12.52.

Complex 12. Colorless crystals (0.61 g, 83%). Mp 222−223 °C. IR (KBr pellets, cm^{-1}): ν 2849 (w), 1629 (s), 1425 (m), 1388 (m), 1304 (w), 1072 (m), 1043 (s), 745 (m), 606 (m). Anal. Calcd for $C_{40}H_{52}N_8O_2SmLi\cdot C_7H_8$: C, 60.94; H, 6.53; N, 12.11. Found: C, 61.01; H, 6.77; N, 12.36.

Complex 13. Pale yellow crystals (0.73 g, 78%). Mp 215−217 °C. IR (KBr pellets, cm^{-1}): ν 2849 (w), 1593 (s), 1416 (s), 1304 (s), 1136 (m), 1034 (m), 745 (m), 615 (m). Anal. Calcd for $C_{40}H_{52}N_8O_2EuLi\cdot C_7H_8$: C, 60.83; H, 6.52; N, 12.08. Found: C, 60.91; H, 6.68; N, 12.05.

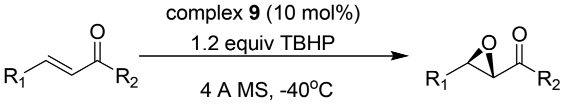
General Synthesis of $(L^4)_2RE^-Li^+(THF)_2$ (RE = Pr(14), Sm(15)). Complexes **14** and **15** were prepared from reactions of $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (0.60 mmol) with the compound H_2L^4 (0.32 g, 1.20 mmol) by employing the procedures similar to those used for preparation of complexes **11**−**13**.

Complex 14. Colorless crystals (0.66 g, 63% yield). Mp 202−204 °C. IR (KBr pellets, cm^{-1}): ν 2867 (w), 1651 (s), 1414 (s), 1370 (m), 1028 (m), 761 (m), 584 (m). Anal. Calcd for $C_{40}H_{52}N_8O_2PrLi$: C, 58.25; H, 6.36; N, 13.59. Found: C, 57.85; H, 6.08; N, 13.35.

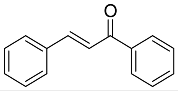
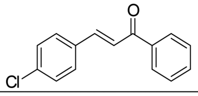
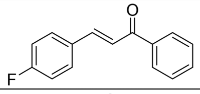
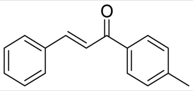
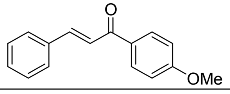
Complex 15. Colorless crystals (0.34 g, 46% yield). Mp 211−214 °C. IR (KBr pellets, cm^{-1}): ν 2845 (s), 1616 (s), 1304 (m), 1417 (m), 1035 (m), 725 (s), 612 (m). Anal. Calcd for $C_{40}H_{52}LiN_8O_2Sm$: C, 57.59; H, 6.28; N, 13.43. Found: C, 57.28; H, 6.31; N, 13.23.

Crystal Structure Determinations. A suitable crystal of complexes **5**−**11**, **13**, and **14** was each mounted in a sealed capillary. Diffraction was performed on a Bruker SMART CCD area detector diffractometer using graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program. All structures were solved by direct methods, completed by subsequent difference Fourier syntheses and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package. All

Table 6. Epoxidation of α,β-Unsaturated Ketones Catalyzed by Complex 9[a]



18 **19**

entry	substrate	products	yield (%)[b]	ee (%)[c]
1		**19a**	65	63
2		**19b**	68	64
3		**19c**	69	65
4		**19d**	64	62
5		**19e**	61	57

[a] Conditions: complex **9** (0.1 mmol), chalcone (1.0 mmol), TBHP (1.2 mmol), THF (2.0 mL). [b] Isolated yields. [c] Enantiomeric excess was determined by the HPLC analysis by using the chiral column.

hydrogen atoms were refined using a riding model. See the Supporting Information for crystallographic parameters and data collection and refinement information.

General Experimental Procedure for Cyanosilylation of Ketones. Under an argon atmosphere, an oven-dried 20.0 mL Schlenk flask equipped with a magnetic stir bar was charged with complex **9** (3.86 mg, 0.0005 mmol), acetophenone (0.58 mL, 5 mmol), and Me_3SiCN (0.75 mL, 6 mmol), and the resulting mixture was stirred under solvent-free conditions for 4 h. At completion, the crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1/20, V/V) as the eluent. The desired 2-trimethylsilyloxy-2-phenylpropanenitrile was obtained as a colorless oil (1.08 g, 99% yield).

General Procedure for the Catalytic Asymmetric Epoxidation of *α*,*β*-Unsaturated Ketones. Under an argon atmosphere, an oven-dried 20.0 mL Schlenk flask equipped with a magnetic stir bar was charged with catalyst (0.1 mmol), *α*,*β*-unsaturated ketone (1.0 mmol), and THF (2.0 mL). The mixture was stirred at room temperature for 5 min, and then the TBHP (1.2 mmol, 0.22 mL) was added in the above solution. The reaction system was stirred for a further 6 h at room temperature and quenched by a Na_2SO_3 aqueous solution. The crude product was purified by column chromatography (ethyl acetate/hexane, 1:10) to obtain the final epoxide product. The enantiomeric excess of epoxides was determined by chiral HPLC analysis.

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b01556.

> Full experimental details, characterization data for compounds **17** and **19**, crystallographic data and refinements for complexes **5**−**11**, **13**, and **14** (PDF)

Accession Codes

CCDC 1846325−1846333 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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